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Critical Review of the Heats of Formation of HNO and Some Related Species

by William R. Anderson

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Abstract

A critical review of the heat of formation of HNO is presented. This molecule and, therefore, its thermodynamics parameters play crucial roles in the chemical mechanism of propellant combustion and NO_x pollutant chemistry. It was found that predissociation experiments, which have gone largely unnoticed for over 15 yr, lead to a significant revision in the recommended value. The new value, $25.6^{+0.6}_{-0.1}$ kcal/mol (298 K; 26.3 kcal/mol at 0 K), is 1 to 2 kcal/mol higher than previous recommendations and has much narrower error limits. Heats of formation of NO, NH₂OH, HNO⁺, and HNO⁻ are also briefly examined, and recommendations are made. Finally, recommendations for future experiments and a brief survey of methods of production of HNO are given in the hope that these will facilitate future studies.

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1. Introduction

The HNO molecule plays crucial roles in the formation of NO_x pollutants during combustion [1], in mechanisms describing the effects of additives used for removal of NO_x from combustion exhaust gases [1], in the conversion of H₂/NO mixtures to final products H₂O and N₂ [2, 3], in the so-called dark zone of solid rocket and gun propellants [3, 4], and in the primary flame zones of such propellants. Under many conditions of interest, several key reactions involving HNO may be significantly reversed or even partially equilibrated. Since reverse rate coefficients are typically calculated using thermodynamics, modeling results involving the detailed chemistry can be very sensitive to input thermodynamic parameters. In particular, the heat of formation of HNO is therefore a very important input parameter in such calculations. This paper reports a critical review that was recently performed on the heat of formation of HNO. In spite of the highly reactive trace nature of this species, it was surprisingly found possible to specify its heat of formation within narrow error limits. Furthermore, the recommendation is about 1 to 2 kcal/mol larger than recommended in two commonly used databases [5, 6, 7].

Previous recommendations for the heat of formation of HNO [5, 6, 7] are based heavily on predissociation results from about 35 yr ago [8, 9]. However, a brief inspection of a more recent result [10] for the predissociation limit revealed a much better theoretical analysis than the earlier works. Also, the resulting heat of formation was significantly larger than that in the earlier works. Consequently, a thorough review of the literature on this heat of formation was in order. As shown in section 2, further spectroscopic studies on HNO and DNO isotopic effects, on kinetics of the recombination reaction H+NO+M → HNO+M, and *ab initio* calculations strongly support the important result that there is no barrier to the reverse reaction. The predissociation results therefore yield an exact equality for the HNO heat of formation rather than a lower limit as usually obtained from such experiments. This fact, in combination with the low error limits of the result, is presented as strong evidence that it is the best value currently available. The recommended heat of formation for HNO may be combined with photoionization mass spectrometric data on NH₂OH to yield a new value for the heat of formation of NH₂OH(g). This and other values are reviewed, and a new

recommendation made. In addition, the heats of formation of the species HNO^+ and HNO^- are discussed.

The information given in the present work first appeared as part of an unrefereed report [3]. Since the publication of Anderson [3], a note pointing out the significance of the predissociation experiments [10] with regard to the HNO heat of formation has appeared [11]. However, Dixon [11] focuses only on the predissociation results as they relate to the HNO heat of formation. The present report covers all literature relevant to this important quantity. Dixon [11] points out that a better value for the NO heat of formation than recommended in Chase et al. [5] is available. This recommendation is accepted and discussed briefly. The change accounts for the slight increase in HNO heat of formation recommended in this work, as opposed to that in Anderson [3]. A few other pertinent studies that have appeared since Anderson [3] are also discussed.

After presentation of the reviews on the heats of formation of the various species, a brief discussion of suggested experiments by which the heat of formation of HNO could be more precisely determined is presented. Then, in order to facilitate both those experiments and others on the kinetics of reactions involving HNO , a brief synopsis of methods found in the literature for making large amounts of this molecule for study is presented. Finally, after a short summary section, a synopsis of thermodynamics results for the species discussed herein and fits of the results to a functional form commonly used in chemical modeling are given in the Appendix. The fits should readily enable usage of the new recommendations in future calculations.

2. Review of Experimental and Theoretical Results Pertaining to the Heat of Formation of HNO

All of the results found in which the heat of formation of HNO was given or from which it could be derived are shown in Table 1. Quantities in parentheses, including error limits in some cases, are results derived in the present work. The new results were either derived using results of the work

Table 1. Results for the Heat of Formation of HNO

Reference	Method	$\Delta H_{f,298}^\circ$ (kcal/mol) ^a
Experimental		
Cashion and Polanyi, 1959 [12]	Threshold of A-X Emission	~26.4
Clement and Ramsay, 1961 [8] Bancroft, Hollas, and Ramsey, 1962 [9]	Predisociation of HNO	$\geq 23.8 (\pm 1.4)$
Clyne and Thrush, 1962 [13]	Kinetics of H+NO+M	-23.8 (± 1.4)
Holmes, 1962 [14]	Kinetics of HI+NO \rightarrow HNO+I	25.3 ± 0.4 ($\leq 24.6 \pm \sim 3$)
Dixon et al., 1981 [10]	Predisociation of HNO	25.6 ± 0.03
Kutina, Goodman, and Berkowitz, 1982 [15]	AP (NH ₂ OH \rightarrow HNO ⁺ +H ₂ +e ⁻)	(21.4 \pm 2.8)
Adams et al., 1989 [16]	Proton Affinity of NO	(25.8 \pm 1.0)
Recent Theoretical		
Bruna and Marian, 1979 [17]	MRD/CI	26.1
Nomura and Iwata, 1979 [18]	SCF/CI	26.3
Adams et al., 1981 [19]	4 MBPT methods	26.4–28.0
Walch and Rohlfing, 1989 [20]	CASSCF/CCI 8e ⁻ , 10e ⁻	26.8, 28.2
Pauzat et al., 1993 [21]	CASSCF/CI	32.3
Diau et al., 1995 [2]	BAC/MP4	23.4
Lee and Dateo, 1995 [22]	CCSD(T)	26.0 ± 0.8
Guadagnini, Schatz, and Walch, 1995 [23]	CASSCF/ICCI	28.0
Recommendations		
JANAF, 1977 [5]		23.8 ^b (± 2.5)
Glushko et al., 1978 [7]		24.4 ± 0.7 (± 2.5)
This work		$25.6^{+0.6}_{-0.1}$

^a Quantities indicated in parentheses were derived in the present work.

^b More recent updates to this database (prior to Anderson [3]) also recommend this older result [6].

cited or the old results were re-evaluated. Re-evaluation may involve use of more recent ancillary data or correction of minor errors in the earlier analyses.

The earliest source of the heat of formation of HNO is from measurement by Cashion and Polanyi [12] of the threshold of $A^1A''-X^1A'$ system emission from the reaction of H with NO. Although that result agrees very well with the present recommendation, it must be recognized that this determination was much more approximate. Cashion and Polanyi did not establish the cutoff of emission. They thought that with increased sensitivity, higher energy transitions might be observed, yielding a larger dissociation energy than the approximate one they recommended.*

Shortly after Cashion and Polanyi's work, Clement and Ramsay [8] and Bancroft, Hollas, and Ramsay [9] performed further A-X emission and absorption studies on HNO. The studies yielded a more precise determination of D_0 than provided in Cashion and Polanyi [12], based upon proof that the excited state was predissociating to H+NO along the ground-state asymptote. An upper limit to the value of D_0 was established by observation of the breakoff points within the coarse rotational K' structure of the molecule. The breakoff points were noted by presence or absence of entire K' subbands within two upper state vibrational levels for HNO and one upper state vibrational level for DNO.[†] From examination of spacing between the K' rotational sublevels involved, it is noted the error limits** in the D_0 determined for HNO must be about 500 cm^{-1} , or 1.4 kcal/mol. Shortly after Clement and Ramsay's [8] publication, Clyne and Thrush [13] pointed out the very important fact that their kinetic studies on $\text{H}+\text{NO}+\text{M} \rightarrow \text{HNO}+\text{M}$ indicated this reaction has a small, negative activation energy. This means the H+NO recombination has little or no barrier, as one would expect, since both species are open-shell. Thus, the predissociation experiments do not just establish a lower bound for the heat of formation of HNO (upper bound for the dissociation energy); the result may

* In the present work, when dissociation or D_0 are discussed in reference to HNO, the terms always refer to breaking the H-NO bond, not the much stronger HN-O bond.)

† HNO is a near symmetric rotor molecule. K' refers to coarsely spaced rotational levels, and J' to more finely spaced rotational levels within the K' levels, in the upper electronic state. Subbands, corresponding to the different K' , form within the overall vibrational bands due to the finer rotational J' structure.

** Not mentioned in Clement and Ramsay [8] or Bancroft, Hollas, and Ramsay [9].

be regarded as an equality. There is much more information establishing lack of any barrier to the recombination reaction, but further discussion of this issue is deferred until later.

Over 15 yr ago, Dixon et al. [10] presented an important reexamination of the A state predissociation, studied via laser induced fluorescence [LIF] experiments. As previously mentioned, this work has surprisingly gone largely unnoticed in the kinetics and thermodynamics communities. This and later related works on both HNO and DNO by Dixon and Rosser [24, 25], Dixon et al. [26], and Petersen [27] include measurement and assignment of the breakoff points of fluorescence vs. the rotational J' quantum number (finer rotational structure) for a large number of the more coarsely spaced vibrational- K' subbands of the molecule. Dixon et al. [10] contains an innovative theoretical analysis of the variation of the centrifugal barrier for rotational quanta K' , J' and the vibrational levels involved for a triatomic molecule. Perhaps even a crude variant of such a centrifugal barrier theory was not available in the early 1960s, or perhaps there were not a large enough number of data on breakoff points of the rotational fine structure within the upper state vibrational levels to permit correction for centrifugal effects. In any case, such a theory was not applied in the earlier work of Clement and Ramsay [8] and Bancroft, Hollas, and Ramsay [9]. The application of a correction for centrifugal barrier and associated extrapolation to the rotationless condition by Dixon et al. [10] must, in principle, yield much higher accuracy for the dissociation energy than in the earlier work. The correction for centrifugal barrier explains the somewhat smaller D_0 reported by Dixon et al. [10] corresponding to the increased heat of formation vs. Clement and Ramsay [8]; Bancroft, Hollas, and Ramsay [9]; Clyne and Thrush [13] (see Table 1). The Dixon et al. [10] result also has a much higher precision than the earlier works for two reasons. First, a much larger number of excited state vibrational- K' levels was used in the later work. Second, and more important, the later work utilized breakoff points in the J' fine structure whose energies are much more closely spaced than those of the K' structure utilized in the earlier work. It is the present recommendation that the previously mentioned heat of formation derived from results of Dixon et al. [10] is therefore clearly the most accurate and precise value currently available. The assignment of error limits is discussed later.

Before leaving the issue of HNO predissociation, an important point should be mentioned. Since Clement and Ramsay's pioneering work in 1961, several works [28, 29, 30] have appeared

concerning the mechanism of the predissociation. Some of these involved alternative suggestions to the final conclusion regarding the mechanism, but it is now firmly established by the most recent theoretical work [30] and the more recent isotopic studies [24] that the predissociation is induced by rotational-electronic coupling. This explains the paradoxical result that a few isolated lines of small upper state J values (corresponding to weak coupling) that have energies *above* the predissociation limit are observed in emission. This effect might, at first, seem confusing in regard to the assignment of the proper limit. However, the origin of these lines is now very well understood.

As stated earlier, Dixon [11] has recently independently pointed out the long-overlooked significance of his group's predissociation studies on HNO. Dixon cites information [31] on the heat of formation of NO from spectroscopic studies (apparently missed in Chase et al. [5]), claiming it is more accurate than the data upon which the recommendation [5] is based. Glushko et al. [7] is in agreement. In Chase et al. [5], the heat of formation of NO is given as 21.6 ± 0.04 kcal/mol (298 K), based upon calorimetry data. Dingle et al. [31] documents a predissociation study on the NO molecule. The dissociation energy, D_0 , was found from study of emission in the $C^2\Pi - A^2\Sigma^+$ system to be 52400 ± 10 cm⁻¹. Strong corroboration for this result may be found in Callear and Pilling [32, 33] and Kley [34]. This D_0 corresponds to a heat of formation (298 K) of 21.82 ± 0.04 kcal/mol (utilizing data on N and O atoms and $H^o - H^o(T)$ functions from Chase et al. [5]; note, these data agree extremely well with the recommendations of Glushko et al. [7]). In predissociation experiments, the starting and final energies of the molecule are well defined by the spectroscopic analysis, especially in the present case of a simple diatomic; the internal energies of the product atoms are also well defined. Although one must always be concerned that there might be a small potential barrier to the predissociation, in the present case, the resulting heat of formation is *larger* than the calorimetry result. Predissociation experiments in which the starting molecule's heat of formation is determined always yield a firm *lower* limit to the heat of formation.* These results must

* Conversely, an upper limit results if a product's heat of formation is determined. This argument also applies to the centrifugal barrier, a subject not mentioned in the previous works relating to NO. However, the predissociation takes place at low J values, between $J = 3$ and 4, and in $v = 0$ of the C state. An estimate of the maximum centrifugal barrier possible for these levels was made, indicating that it is just below the threshold of significance to the recommendation. Should future studies involving predissociation result in significant reduction of the error limits, this effect might require further consideration.

therefore be regarded as strong evidence that the slightly smaller result from calorimetry experiments is too low. The recommendation of the predissociation results in computing the heat of formation of NO by Glushko et al. [7] and Dixon [11] is therefore accepted. This new ancillary datum has been utilized in the present work, thus accounting for minor changes in results for HNO and related species vs. Anderson [3].

Upon careful scrutiny, it was found that most of the other works cited in Table 1 agree with the recommendation. These are discussed in the following paragraphs.

The result of Holmes [14] was based upon measurements of the activation energy for the endothermic reaction $\text{HI} + \text{NO} \rightarrow \text{HNO} + \text{I}$ and an assumption that the reverse reaction is barrierless. Because the reverse reaction actually could have a barrier, the resulting heat of formation must be regarded as an upper limit. The present re-evaluation of the heat of formation, result given in Table 1, took into account more recent values of the heats of formation of the other species [5]. The error limit in the activation energy given by Holmes is only 0.4 kcal/mol, implying fairly narrow error limits in the heat of formation. This result would therefore appear not to support the recommended value. However, Holmes' paper is extremely short and sketchy regarding exactly what was done in the measurements and analysis. Additionally, the experiments were only performed over a modest range in $1/T$. Finally, there is no corroborative kinetics evidence on this reaction from other laboratories. It is well-known practice to require such evidence in critical evaluation of kinetics results before acceptance of such narrow error limits, particularly for E_a values in cases involving short temperature ranges. The reason is that, frequently, in kinetics studies of elementary reactions, it is altogether too common to observe reported differences in rate coefficients from different, good groups that are well outside the combined error limits. A large number of effects (e.g., impurities) can account for systematic variations. Consequently, because of the sketchy nature of the documentation and the lack of support from other laboratories regarding the rate coefficient, this result is not at all convincing evidence that the predissociation results are in error. Estimated error limits of ~3 kcal/mol are assigned for the resulting heat of formation.

Results of either Kutina, Goodman, and Berkowitz [15] or of Adams et al. [16] can be combined with other data to yield the heat of formation of the HNO^+ ion (see later). These results were combined with the ionization potential of HNO , 10.18 ± 0.01 eV, to yield the resulting HNO heats of formation given in the table. This ionization potential was first obtained by Baker et al. [35]. A strongly supportive result, identical in both magnitude and error limits after rounding to the same number of significant digits, was obtained by a different method in the recent work of Kuo et al. [36].* As added support, one notes Baker et al. [35] also measured the ionization potential of DNO , obtaining 10.20 ± 0.01 eV. A much earlier measurement of this quantity, 10.29 ± 0.14 eV, was obtained by Kohout and Lampe [38]. This result agrees well with Baker et al. [35] considering the wider error limits.

Adams et al. [16] presented a measurement of the proton affinity of NO , 127 ± 1 kcal/mol at 300 K. In the present work, the heat of formation of HNO^+ was obtained from this proton affinity using the heat of formation of NO discussed previously and the heat of formation of H^+ from Chase et al. [5]. Conversion of the result to 0 K was accomplished using $\text{H}^\circ - \text{H}^\circ(T_r)$ functions for the reference elements from the JANAF tables [5] and equations from the introductory material for $\text{H}^\circ - \text{H}^\circ(T_r)$ in Chase et al. [5] to determine this function for HNO^+ . *Ab initio* calculations of the vibrational frequencies of HNO^+ from Bruna and Marian [39] were used in the latter calculation. These frequencies were first multiplied by 0.9, an average correction found necessary [40] to get good agreement between such *ab initio* results and experiments in cases in which, unlike this one, measurements exist. Note the thermodynamic results are not very sensitive to the choice of this factor.[†] The resulting HNO^+ heat of formation, combined with the aforementioned ionization

* In support of their result, Kuo et al. [36] derived two values for the heat of formation of HNO^+ utilizing data on the exothermicities of two ion-molecule reactions, which they claim were measured by Burt et al. [37]. They then compared these to results obtained utilizing their measured ionization potential as one input datum. However, the energies of those reactions were apparently *not measured* by Burt et al. [37] as Kuo et al. [36] thought. Instead, the *rate coefficients* of the two pertinent reactions were obtained by a flow technique. In fact, the energetics of such exothermic reactions probably cannot be determined via kinetics experiments. The reaction energies quoted in Kuo et al. [36] were given in Table 1 of Burt et al. [37] with no comment regarding their source, and with no error limits. Consequently, little meaning can be assigned to those comparisons.

† It is to be emphasized that it was realized a serious error can be made for ions if the proper handling of the separated electron is not considered in converting temperatures. Since, by the convention used in Chase et al. [5] the $\text{H}^\circ - \text{H}^\circ(T_r)$ functions for H^+ include the heat absorbed by the separated electron, $(5/2)RT$, this term must also be included in the similar function determined for HNO^+ .

potential [35, 36], yields the heat of formation for HNO given in Table 1. The result is in excellent agreement with the present recommendation.

The heat of formation given for HNO^+ by Kutina, Goodman, and Berkowitz [15], 256.8 ± 1.4 kcal/mol (0 K), leads to an HNO heat of formation much lower than that recommended (see Table 1).^{*} Kutina, Goodman, and Berkowitz [15] obtained the ion's heat of formation by combining their measurement of the appearance potential for the reaction $\text{NH}_2\text{OH} \rightarrow \text{HNO}^+ + \text{H}_2 + \text{e}^-$, 11.56 ± 0.06 eV, with the heat of formation of NH_2OH , -9.738 kcal/mol (0 K), derived by the authors from calorimetry data in a manner analogous to that used in Glushko et al. [7]. Now, it immediately occurs that the products could be internally excited, thus leading to a systematic error. However, upon further consideration, one finds this would lead to an erroneously *large* appearance potential, hence, too *large* a value for the heat of formation of HNO. In contrast, the result of the work [15] is much too low. As discussed previously, the analysis of Dixon et al. [10] is very convincing.[†] It is in reasonable agreement with most of the other results. The result given in the table derived from Kutina, Goodman, and Berkowitz's [15] appearance potential is therefore clearly incorrect. However, their measurement and analysis of this appearance potential seems straightforward and convincing, especially since there are no apparent spectral interferences. The ionization potential from Baker et al. [35] and Kuo et al. [36] is also convincing, particularly since, as mentioned previously, its use in combination with the NO proton affinity leads to an HNO heat of formation in good agreement with most of the other results (see Table 1). The currently accepted heat of formation of $\text{NH}_2\text{OH(g)}$, the other datum used in this approach to calculate the HNO heat of formation, is therefore drawn into question.^{**} A brief review has shown that all prior measured or calculated values of this quantity have fairly large error limits. It is probably best, therefore, to regard the heat of formation of NH_2OH , rather than HNO, as the quantity to be determined in combining these appearance and ionization potential data. This subject is discussed later.

^{*} In deriving the associated error limit in the table, the error in heat of formation of NH_2OH was also considered. This error was taken from Glushko et al. [7].

[†] The reader is reminded that this result must be regarded as yielding a firm lower limit to the heat of formation of HNO, even if one does not accept the notion that there is no barrier to the recombination reaction $\text{H} + \text{NO}$.

^{**} It should be noted that J. Berkowitz [41] agrees with this conclusion.

The recommended value of the HNO heat of formation is, reassuringly, in reasonable agreement with most of the recent theoretical results (see Table 1). It is believed the most accurate methods were used by Adams et al. [19], Walch and Rohlffing [20], Lee and Dateo [22], and Guadagnini, Schatz, and Walch [23]. Results from such methods are generally within about 2–3 kcal/mol of the best experimental results for closed-shell species. The results from these sources are thus in reasonable agreement with the recommendation. Lee and Dateo, in particular, claim smaller error limits for their result than usual for *ab initio* work. This claim of high precision may result because they focused efforts primarily upon the HNO heat of formation (not all the *ab initio* studies did), because they used more than one calculational technique and achieved good agreement between results, and/or because the calculational methods have been tested against experiment for a wide variety of molecules (see the discussion in Lee and Dateo [22]). In any case, their result is in excellent agreement with the present recommendation based upon experiment.

Turning now to the prior recommendations, both are significantly smaller than the present recommendation. The JANAF recommendation [5, 6], which is used in the Sandia thermodynamics database [42], is from the older predissociation result [8, 9] combined with the kinetic observations of Clyne and Thrush [13], which indicate that there is no barrier to the recombination. As should now be abundantly clear, this should be replaced with the newer result of Dixon et al. [10] because of the latter's investigation of the breakoff points in the closely spaced J' structure and the compelling analysis thereof. The recommendation from Glushko et al. [7] was obtained by averaging the old predissociation result [8, 9, 13] with the result of Holmes [14]. It should be noted that the error limits suggested by Glushko et al. [7] seem altogether too optimistic. It would seem that reasonable error limits for both of the values being averaged should be about 1.4–3 kcal/mol. It is thus seen that the small error limit is likely the result of a coincidental close agreement in the two results being averaged; a more reasonable error limit for their recommendation would be about 2–3 kcal/mol. Thus, when consideration is given to the sources of the earlier recommendations and the appropriate associated error limits, they are seen to be in reasonable agreement with the present, more precise, recommendation.

As promised earlier, a discussion of work supporting the notion that the recombination reaction $H+NO+M \rightarrow HNO+M$ is barrierless is now given. The discussion was saved until this point because it leads naturally into a defense of the error limits given herein for the recommended HNO heat of formation. There are several facts from different types of studies leading to this important conclusion: (1) kinetics experiments on the recombination reaction; (2) results from some of the ab initio studies, and (3) consideration of isotopic substitution effects on the predissociation results. These and the recommended error limits are considered in the next few paragraphs.

There are kinetics studies by two groups, Clyne and Thrush [13] and Atkinson and Cvitanovic [43] and Oka, Singleton, and Cvitanovic [44], wherein the temperature dependence of the recombination reaction $H+NO+M \rightarrow HNO+M$ has been studied so that an effective activation energy can be inferred. In the case of the Cvitanovic group, the more recent study [44] is taken as the final result. The two sets of experiments cover the region from $231 < T < 704$ K for $M = H_2$. The agreement between results in the region of overlap, $298 K < T < 477$ K, is excellent. Furthermore, when data of either study is fitted to the form $k = A \exp(-E_a/RT)$, the resulting activation energy is about -0.65 kcal/mol [44]. Now, in a case where a reaction exhibits a negative activation energy, the corresponding rotationless reaction barrier must be nearly zero. However, though it seems improbable, the possibility of a slight barrier, say a few tenths of a kcal/mol, cannot be entirely ruled out on the basis of experiment. This is the case because the fitted activation energy arises from the difference between average energy of reacting complexes at the transition state minus average energy of reactants [45]. If the reacting complexes are internally cold, the distribution of internal energies vs. temperature can vary in such a way as to produce, for example, a negative activation energy in the fitted results, as observed often for radical-radical recombination reactions, such as $H+NO$. Typically, this means the barrier to reaction is nearly zero. Indeed, the barrier must be small, but there is no obvious reason it has to be exactly zero.

The theoretical results of Adams et al. [19] indicate a barrier of about 0.6 kcal/mol exists at 4.0 \AA H-N distance in the H-NO dissociation channel.* Calculations of Walch and Rohlfing [20]

* The other geometric parameters were properly allowed to reoptimize during the dissociation in those calculations.

and Guadagnini, Schatz, and Walch [23], which in principle should be more accurate, indicate there is no barrier at all. In addition, those workers feel intuitively there should be no long range attractive interactions in the potential. However, their actual calculations, unfortunately, extended only to 2.6 Å. Therefore, it is deemed prudent to consider that the 0.6-kcal/mol barrier may actually exist and use this notion in determination of error limits.

As pointed out by Dixon and Rosser [24], the observed difference in dissociation energies of HNO and DNO determined from the breakoff points in the rotational branch structure is, within error limits, identically equal to the difference in HNO and DNO zero-point energies. This would not be possible if there is a very significant barrier in the dissociation channel because the difference in H or D atom vibrational motion would contribute an additional difference to the respective dissociation energies. Using simple harmonic oscillator calculations and equations in Dixon and Rosser [24], one can show, however, that a barrier of only a few tenths of a kcal/mol still cannot be ruled out, particularly if the exit channel is very broad.

The preceding ideas lead to a discussion of the error limits in the recommended heat of formation. A notion of how much the predissociation model of Dixon and Rosser [24] affects the extrapolation to zero rotation can be obtained by comparing their results for DNO with the similar results of Petersen [27]. Petersen performed the extrapolation, as is often done, by the simple expedient of fitting a straight line to the typical plot of rotational energies at the breakoff points vs. $J(J+1)$ for the various upper state vibronic sublevels and extending it to $J=0$. This procedure leads to a dissociation energy that is ~0.1 kcal/mol smaller than that of Dixon and Rosser [24], whose more theoretically correct approach results in a line with upwards curvature. This difference is considered a conservative estimate of the systematic error, which could be induced by an error in the model of centrifugal barrier effects; it is used as the lower error limit of the present heat of formation recommendation. If the aforementioned concern about a possible slight barrier in the H-NO dissociation channel can eventually be alleviated, then the upper error limit would also become 0.1 kcal/mol. This upper error limit would result because it is just barely conceivable that the predissociation is taking place, albeit slowly, at the last observed emitting J' level in each vibrational- K' subband. In fact, lifetime measurements performed on the (1,0,0) $K'=4$ vibronic sublevel show

that for the last observed emission, at $J'=11$, the fluorescence lifetime is significantly shorter than for lower levels [26], evidently due to predissociation. However, a more conservative estimate is recommended for the upper error limit for the present. This is obtained using the calculated barrier of Adams et al. [19] in the ground-state exit channel for the predissociation. This 0.6-kcal/mol barrier is large enough that it completely overshadows the possible error due to uncertainty in threshold J level. The final recommended value is thus $25.6^{+0.6}_{-0.1}$ kcal/mole (298 K). It is to be emphasized that these error limits seem conservative.

In regard to two other species closely related to HNO, it should be noted that the positive and negative HNO ion heats may be easily derived from the HNO heat of formation and ancillary data. As previously mentioned, for the positive ion, the heat of formation was obtained using the NO proton affinity from Adams et al. [16] (just prior to determination of the heat of formation of HNO). The result thus obtained for the ion was 261.2 ± 1.0 kcal/mol (0 K). Alternatively, one may obtain results with higher precision by using the heat of formation of HNO recommended herein as an input parameter. This value, when combined with the ionization potential [35, 36], yields 261.1 ± 0.6 kcal/mol (0 K), in excellent agreement with the previous result obtained using the proton affinity measurement. The weighted average [46] of these two experimental results, 261.1 ± 0.5 kcal/mol (0 K), is the final recommendation of this study. The recommendation is in excellent agreement with the MRD-CI *ab initio* result, 260.7 ± 2 kcal/mol, from Bruna and Marian [39]. Turning now to the negative ion, one obtains its heat of formation by combining the heat of formation of the neutral molecule with the electron affinity, 0.338 ± 0.015 eV, measured by Ellis and Ellison [47]. The result is 18.5 ± 0.7 kcal/mol (0 K).

As mentioned earlier, a brief review of the heat of formation of $\text{NH}_2\text{OH(g)}$ was also performed. As discussed by Glushko et al. [7], and later similarly by Kutina, Goodman, and Berkowitz [15], this quantity can be derived from calorimetry measurements on the heat of solution of hydroxylamine and the enthalpy of its reactions with a number of species in solution (see Glushko et al. [7] regarding these works), coupled with sublimation data on hydroxylamine from Back and Betts [48]. Using these data, Glushko et al. [7] recommend -9.6 ± 2.4 kcal/mol for the heat of formation of $\text{NH}_2\text{OH(g)}$ (0 K; -12.0 ± 2.4 kcal/mol at 298 K). Alternatively, by combining the appearance

potential for $\text{NH}_2\text{OH} \rightarrow \text{HNO}^+ + \text{H}_2 + \text{e}^-$ [15] together with the heat of formation of HNO recommended in the present work and the HNO ionization potential [35, 36], one finds the value -5.5 ± 1.5 kcal/mol for the heat of formation of $\text{NH}_2\text{OH(g)}$ at 0 K (-7.9 ± 1.5 kcal/mol at 298 K). Two theoretical calculations of this quantity were found [49–53]. Wiberg's study [49] included a calculation of the bond energy $D_0(\text{NH}_2\text{--OH})$ using the Pople G1 method. This bond energy may be combined with heats of formation of NH_2 [54] and OH [5] to yield the heat of formation of NH_2OH . The result is -8.2 kcal/mol at 0 K (-10.6 kcal/mol at 298 K). Sana et al. [50, 51]; Leroy, Sana, and Wilante [52]; and Sana and Leroy [53] used four similar MP4 methods to calculate the heat of formation of NH_2OH and a number of other compounds, all yielding comparable results. The value from the most recent of these works [53], -11.7 kcal/mol (298 K), is taken as the final result of that group. The *ab initio* calculations seem to better support the calorimetric than the spectroscopic measurement. However, error limits for the *ab initio* results are estimated to be about 3 kcal/mol; thus, error limits in the *ab initio* results overlap those of the spectroscopic, as well as the calorimetric result. No apparent reason could be found to favor any of these four techniques. Therefore, the weighted average [46], -9.6 ± 2.2 kcal/mol at 298 K, is the recommendation of the present study. Clearly further work on this quantity is warranted.

3. Recommendations for Future Work

In this section, a brief description is given of possible experiments that could be performed to increase the precision in the heat of formation of HNO. Similar experiments might also be performed on NH, and possibly any other troublesome radical with a predissociation available for study.

The main feature of the predissociation phenomenon that makes it very attractive for thermodynamic determinations is that both the initial and final states of the probed molecule are picked out at very precisely known energies. This is clearly not the case for a broadband absorption where the spread in initial energies severely complicates data analysis. The remaining difficulty with the predissociation approach is that the energies of the fragments are not precisely known. However,

it is quite conceivable that these energies could be measured. In the case of HNO, one possibility is to perform a pump-probe experiment with an LIF probe beam interrogating the NO fragment. An experiment along these lines has been attempted by Dixon [55] without success, due to the presence of background NO in the sample cell. Of course, the ultimate in sophistication would be to use a molecular beam (but not supersonic because high J levels are required) intersected by a pump laser beam, pulsed to yield time resolution, and a second LIF probe for NO located some distance away. This experiment would directly yield the full gamut of information on translational, rotational, and vibrational energy of the products. An alternative is to use a probe of the H atom to measure the product translational energy and attempt to infer the NO internal energy from modeling of the photodissociation, which may be possible for this small molecule, and/or from measurements of the spread in H atom velocities.*

It would appear that these ideas have more universal application than just to the HNO molecule. As another example, consider the NH radical. It is well known that the $c^1\Pi$ state of this radical predissociates [57]. Thus, pumping of a suitable transition in the $c^1\Pi-a^1\Delta$ electronic system would lead to formation of H and N atoms, which could be detected by any of a number of methods to yield the translational energy of the products. The result would be fairly straightforward to analyze. The major difficulty might be in preparation of the $a^1\Delta$ state molecules. This, however, can be done by photolysis of HN_3 [58, 59]. The heats of formation of both NH and HNO are so important in combustion models that the expenditure of effort seems warranted. Design of an experiment should take into account, though, that unless it appears that the resolution is sufficient to result in a precision of better than ~ 1 kcal/mol, there seems little point to pursue it for either of these species solely to obtain thermodynamic information. Their heats of formation are already known within such limits.

To facilitate studies on the thermodynamics and kinetics of HNO, a brief survey of techniques for production of the molecule, which is not purported to be exhaustive, is now given. At least five methods have been used, with a variety of simple modifications, to make HNO in sufficient quantity for spectroscopic study. The first, and probably most commonly used, especially in the earliest

* The latter idea arose in conversations between the author and Wittig [56].

studies, is the simple recombination of H atoms with NO; that is, $H+NO+M \rightarrow HNO+M$. It seems likely this reaction is what was occurring in the pioneering spectroscopic study of Dalby [60], who photolyzed a mixture of NH_3/NO and obtained sufficient absorption in the A-X system to study the rotational structure in detail. The H atoms can be obtained from a variety of sources. The second technique (also mentioned by Dalby) is photolysis of a suitable precursor. Dalby mentions several nitro or nitrite molecules he used and states nitromethane produced the strongest signal. Unfortunately, it is impossible, at present, to be sure whether the HNO is a direct photolytic product of even the nitrites. In fact, it probably is not the main product [61]. Note that all of Dalby's experiments were performed on a time scale sufficient for many reactions to occur. A third technique, pioneered by Yamada et al. [62, 63] and utilized more recently by Kuo et al. [36], is through the production of O atoms (in their case, either by discharge of O_2 or by reaction of N atoms with NO) followed by their reaction with a mixture of olefins and NO. Yamada et al. [62, 63] and Kuo et al. [36] attribute production of HNO to $O+olefin \rightarrow HCO+alkyl\ radical$, followed by $HCO+NO \rightarrow HNO+CO$. Although the latter reaction is known to be very fast, and the former likely has an appreciable rate at room temperature [64], there is clearly some doubt as to whether HCO is the main direct product of the former. The overall rate of $O+olefin$ is quite fast [64], but the product distribution apparently is not well established. The actual HNO production mechanism could well involve formation of other products that are converted to HCO or, perhaps, even an entirely different route. The uncertainty in the mechanism could make tuning of conditions difficult. One notes the S/N ratio in Yamada's [62, 63] results was not high, suggesting the HNO concentration was also not high. However, the method clearly has some merit. A fourth technique, discovered by Sanders et al. [65], is through the very fast reaction of CH_3O (formed in their case by photolysis of CH_3ONO) with NO. The S/N ratio achieved in that work was very high for LIF experiments on HNO at the time and remains amongst the highest known (see figures in Sanders et al. [65]). Finally, the fifth method is via pyrolysis of the adduct of HNO with 9,10 dimethyanthracene. This method has produced very high concentrations. It was pioneered by Kirby and Sweeny [66] and Corrie et al. [67] and has been used extensively by the Ottawa and Bristol groups (e.g. [10, 24–27]).

A major difficulty of all these HNO preparation techniques is that most involve fairly large concentrations of other species. These would likely interfere with dynamical studies of

predisociation or kinetic studies because of secondary collisions or reactions. What needs to be developed is a method for photolytic production using a thermally stable precursor. One possibility is infrared multiphoton photolysis of a nitrite (e.g. C_2H_5ONO).^{*} The 9,10 dimethylantracene compound mentioned in the preceding paragraph might be an even more likely multiphoton photolysis precursor, if it has a significant partial pressure, because it has already been shown to yield HNO upon thermal excitation.

4. Summary

A critical review of the heat of formation of HNO has been completed. The new recommendation is significantly larger than previous recommendations and the error limits are much smaller. This outcome is primarily due to the discovery of the most recent results from predisociation experiments and ancillary works on the molecule, which indicate that the back reaction has nearly zero barrier. The most recent predisociation results have gone largely unnoticed for over 15 yr. Heats of formation of NO, NH_2OH , HNO^+ , and HNO^- were also briefly examined, and recommendations were made. To facilitate usage of these new results in future calculations, synopsis tables of the newly recommended heats of formation, thermodynamic parameters needed for detailed chemical modeling, and fitted constants to the functional form recommended in the NASA-Lewis studies [68-70] are given for the neutral species in the Appendix. Finally, recommendations for future experiments and a brief survey of methods of production of HNO are given.

^{*} C_2H_5ONO is suggested rather than the simpler CH_3ONO because it seems probable there is a smaller energetic barrier to HNO elimination for the former, due to the possibility of a five-center transition state.

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Appendix:

Tabular Synopsis of Results and Fits to NASA-Lewis Format

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In the Appendix, a synopsis of the results is given in three tables. In Table A-1, the final recommendations for heats of formation of the five species mentioned in the text are reiterated. In Table A-2, a synopsis of the thermodynamic data needed for chemical modeling calculations for three of these species is given. These include the heats of formation at 298, entropy, S° , at 298, and $C_p(T)$, the temperature dependent heat capacity function. Data for the S° and $C_p(T)$ functions were obtained for HNO and NO from Chase et al.¹ and for NH₂OH from Glushko et al.² (Data on S° and $C_p(T)$ functions were not readily available for the other two species.) Fits of the results in Table A-2 to the 14-parameter expression recommended by the NASA-Lewis group³ are given in Table A-3. This 14-parameter expression is of the older type used by that group. The older type expression is used in many computer codes, such as CHEMKIN-based codes. For explanation of the various constants and their arrangement in the table, see Gordon and McBride³. The fits were performed using the THERMFIT computer code of Ritter.⁴ It should be noted that the latter code divides regions of applicability of the constants at a point other than 1,000 K, as common in many earlier fitting approaches. The temperature (K) at the point dividing the two regions is the last number in the first line for each species. Users should take caution that their codes do not assume this temperature to be 1,000 K.

¹ Chase, Jr., M. W., Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud. "JANAF Thermochemical Tables Third Edition." *Journal of Physical and Chemical Reference Data*, vol. 14, suppl. no. 1, 1985.

² Glushko, V. P., L. V. Gurvich, G. A. Bergman, G. A. Khachkurov, V. A. Medvedev, I. V. Veyts, and V. S. Yungman. *Thermodynamic Properties of Individual Substances, 4th edition*, vol. 1, parts 1 and 2, Hemisphere, NY, 1989.

³ Gordon, S., and B. J. McBride. "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations." NASA-SP-273, NASA Lewis Research Center, Cleveland, OH, March 1976.

⁴ Ritter, E. R. "THERM: A Computer Code for Estimating Thermodynamic Properties for Species Important to Combustion and Reaction Modeling." *Journal of Chemical Information and Computer Sciences*, vol. 31, p. 400, 1991.

Table A-1. Recommended Heats of Formation From the Present Study

Species	$\Delta H_{f,0}^\circ$ (kcal/mol)	$\Delta H_{f,298}^\circ$ (kcal/mol)
HNO	$26.3^{+0.6}_{-0.1}$	$25.6^{+0.6}_{-0.1}$
NO	21.70 ± 0.04	21.82 ± 0.04
NH ₂ O	-7.2 ± 1.5	-9.6 ± 1.5
HNO ⁺	261.1 ± 0.6	260.4 ± 0.6
HNO ⁻	18.5 ± 0.7	—

Table A-2. Thermodynamic Data for HNO, NO, and NH₂OH

Species	$\Delta H_{f,298}^\circ$	S_{298}°	C_p (300)	C_p (400)	C_p (500)	C_p (600)	C_p (800)	C_p (1,000)	C_p (1,500)
HNO	25.60	52.75	8.29	8.79	9.34	9.87	10.77	11.45	12.51
NO	21.82	50.37	7.13	7.16	7.29	7.47	7.83	8.12	8.55
NH ₂ OH	-9.60	56.45	11.14	12.81	14.26	15.48	17.47	19.11	22.12

Table A-3. NASA-Lewis Fitted Parameters for Thermodynamic Data of HNO, NO, and NH₂OH^a

```

HNO          WRA4/11/97H  1N  10  1   0G  300.000  5000.000 1514.000  01
  4.10879877E+00 2.44877874E-03-8.43604912E-07 1.31599572E-10-7.66040844E-15  2
  1.13279874E+04 1.98856114E+00 3.38462154E+00 2.38366435E-03 1.28311921E-06  3
  -1.75172122E-09 4.65057041E-13 1.17605791E+04 6.51018773E+00 4
NO          WRA4/11/97N  10  1   0   0G  300.000  5000.000 1410.000  01
  3.32489811E+00 1.01455800E-03-2.99440328E-07 3.95649227E-11-1.93954545E-15  2
  9.91755482E+03 6.05812181E+00 3.19760951E+00 1.19985320E-03-3.69858069E-07  3
  3.48038232E-11 2.96159355E-15 9.97787961E+03 6.78947372E+00 4
NH2OH        WRA4/23/97H  3N  10  1   0G  300.000  5000.000 1386.000  01
  5.19648293E+00 6.57454909E-03-2.25540588E-06 3.50698747E-10-2.03635960E-14  2
  -7.12289663E+03-3.98850915E+00 2.43165806E+00 1.28115495E-02-8.29345472E-06  3
  3.33532343E-09-6.23855863E-13-6.05886049E+03 1.10756758E+01 4

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^a Data are in an 80-column format, suitable for input to user computer codes formatted for NASA-Lewis fits.³

³ Gordon, S., and B. J. McBride. "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations." NASA-SP-273, NASA Lewis Research Center, Cleveland, OH, March 1976.

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6. AUTHOR(S) William R. Anderson			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WM-PC Aberdeen Proving Ground, MD 21005-5066		8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-1557	
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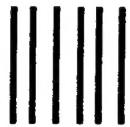
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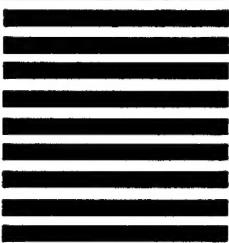
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